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=> s (irradiat? or photopolymeri?)(s)(block(3a)copolymer?) 2004 (IRRADIAT? OR PHOTOPOLYMERI?)(S)(BLOCK(3A) COPOLYMER?) L1

=> s ((polymer# or copolymer#)(4a)(block# or segment#))(s)((ortho? or meta? or para?)(3a)(alkyl? or methyl? or ethyl?))

2383 ((POLYMER# OR COPOLYMER#) (4A) (BLOCK# OR SEGMENT#))(S)((ORTHO? OR META? OR PARA?) (3A) (ALKYL? OR METHYL? OR ETHYL?))

=> s 11 and 12 45 L1 AND L2

=> s ((polymer# or copolymer#)(4a)(block# or segment#))(s)(conjugated dien? or butadiene or 1,3-butadiene or isoprene)

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47954 ((POLYMER# OR COPOLYMER#)(4A)(BLOCK# OR SEGMENT#))(S)(CONJUGATED DIEN? OR BUTADIENE OR 1,3-BUTADIENE OR ISOPRENE)

=> s 13 and 14

L5 9 L3 AND L4

=> d 15 1-9 ibib abs

ANSWER 1 OF 9 USPATFULL on STN

ACCESSION NUMBER: 2007:236812 USPATFULL

TITLE: Tear and abrasion resistant expanded material and

reinforcement

INVENTOR(S): Scanlon, John James, Wilmington, DE, UNITED STATES

Scanlon, Catherine Ann, Wilmington, DE, UNITED STATES

NUMBER KIND DATE _____ US 20070207186 A1 20070906 US 2007-713361 A1 20070303 (11) PATENT INFORMATION: APPLICATION INFO.:

NUMBER DATE _____

US 2006-779128P 20060304 (60) PRIORITY INFORMATION:

DOCUMENT TYPE: Utility APPLICATION FILE SEGMENT:

LEGAL REPRESENTATIVE: John J. Scanlon, 1308 Hillside Blvd, Wilmington, DE, 19803, US

NUMBER OF CLAIMS: 21

NUMBER OF CLAIMS: 1 EXEMPLARY CLAIM:

NUMBER OF DRAWINGS: 11 Drawing Page(s)

LINE COUNT: 7752

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

The present invention is a more durable expanded material that enables thinner wall thicknesses and a more flexible reinforcement suitable for stenting. The present invention is especially useful in the construction of grafts, stents, and stent-grafts which are used, for example, in repairing or replacing blood vessels that are narrowed or occluded by disease, aneurismal blood vessels, or other medical treatments. The inventive material and configurations allow expansion or contraction in size or adjustment in size in an incremental manner so that the optimum size, shape, and fit with other objects can be obtained. The present invention is also optionally capable of more accurately delivering one or more active ingredients such as drugs over longer periods of time. The present invention optionally includes surface modifications and additives that increase the surface adhesion of active ingredients, coatings, or combinations thereof. Finally, the present invention optionally includes growing cells on the inventive material so that the expanded material, reinforcement, or combinations thereof are useful, for example, in producing lab-grown blood vessels or organs.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 2 OF 9 USPATFULL on STN

ACCESSION NUMBER: 2005:275365 USPATFULL

TITLE: Photocurable compositions and flexographic printing

plates comprising the same

INVENTOR(S): Clair, David J. St., Houston, TX, UNITED STATES

Hansen, David R., Houston, TX, UNITED STATES Dubois, Donn A., Houston, TX, UNITED STATES

PATENT ASSIGNEE(S): KRATON Polymers U.S. LLC, Houston, TX, UNITED STATES

(U.S. corporation)

NUMBER KIND DATE ______ PATENT INFORMATION: US 20050239930 A1 20051027 US 7241540 B2 20070710 APPLICATION INFO.: US 2004-832733 A1 20040427 (10)

DOCUMENT TYPE: Utility FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: KRATON POLYMERS U.S. LLC, WESTHOLLOW TECHNOLOGY CENTER,

3333 HIGHWAY 6 SOUTH, HOUSTON, TX, 77082, US 16

NUMBER OF CLAIMS: EXEMPLARY CLAIM: 1 550 LINE COUNT:

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

The present invention relates to photocurable compositions for use in flexographic printing plates comprising selectively hydrogenated

block copolymers of conjugated

dienes and monoalkenyl arenes and flexographic printing plates

made from the same. The block copolymers, either

linear or radial, have terminal blocks of unsaturated conjugated

diene. The block copolymer is further

comprised of monoalkenyl arene blocks and hydrogenated

conjugated diene blocks. The compositions exhibit exceptional improvement in degree of cure over comparative selectively

hydrogenated block copolymers.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 3 OF 9 USPATFULL on STN

ACCESSION NUMBER: 93:91503 USPATFULL

TITLE: Electrophotographic lithographic printing plate

precursor

INVENTOR(S): Kato, Eiichi, Shizuoka, Japan
PATENT ASSIGNEE(S): Fuji Photo Film Co., Ltd., Kanagawa, Japan (non-U.S.

corporation)

NUMBER KIND DATE PATENT INFORMATION: US 5258249 19931102 APPLICATION INFO.: US 1991-779915 19911021 DISCLAIMER DATE: 20101019 19911021 (7)

NUMBER DATE _____

PRIORITY INFORMATION: JP 1990-302480 19901109

DOCUMENT TYPE: Utility
FILE SEGMENT: Granted

PRIMARY EXAMINER: McCamish, Marion E.
ASSISTANT EXAMINER: Crossan, Stephen C.
LEGAL REPRESENTATIVE: Sughrue, Mion, Zinn, Macpeak & Seas

NUMBER OF CLAIMS: 11
EXEMPLARY CLAIM: 1
1554

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

An electrophotographic lithographic printing plater precursor which utilizes an elecrophotographic light-sensitive material comprising a conductive support having provided thereon at least one photoconductive layer containing photoconductive zinc oxide and a binder resin, wherein the binder resin contains at least one AB block copolymer composed of an A block comprising a polymer component corresponding to a monofunctional monomer containing a functional group which has at least one atom

selected from a fluorine atom and a silicon atom and is capable of forming at least one hydrophilic group selected from a sulfo group, a phosphono group, a carboxy group and a hydroxy group through decomposition, and a B block containing at least a polymer component represented by general formula (I) described herein.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 4 OF 9 USPATFULL on STN

ACCESSION NUMBER: 88:22002 USPATFULL

TITLE: Dry ammonium nitrate blasting agents

INVENTOR(S): Bachman, Harold E., Summit, NJ, United States

Totman, Ralph S., Ft. Saskatchewan, Canada

PATENT ASSIGNEE(S): Exxon Chemical Patents Inc., Linden, NJ, United States

(U.S. corporation)

NUMBER KIND DATE _____ US 4736683 19880412 US 1986-893406 19860805 (6) PATENT INFORMATION:
APPLICATION INFO.: DOCUMENT TYPE: Utility FILE SEGMENT: Granted
PRIMARY EXAMINER: Nelson, Peter A.

LEGAL REPRESENTATIVE: Murray, Jr., J. B.

NUMBER OF CLAIMS: 37 EXEMPLARY CLAIM: 1 NUMBER OF CLAIM: 1379

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

The invention relates generally to explosives, and more particularly to dry ammonium nitrate-fuel oil based explosives, containing a high molecular weight polymer characterized by a high stringiness factor.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 5 OF 9 USPAT2 on STN

ACCESSION NUMBER: 2005:275365 USPAT2

Photocurable compositions and flexographic printing

plates comprising the same

INVENTOR(S): St. Clair, David J., Houston, TX, UNITED STATES

Hansen, David R., Houston, TX, UNITED STATES Dubois, Donn A., Houston, TX, UNITED STATES

Kraton Polymers U.S. LLC, Houston, TX, UNITED STATES PATENT ASSIGNEE(S):

(U.S. corporation)

NUMBER KIND DATE _____ PATENT INFORMATION: US 7241540 B2 20070710
APPLICATION INFO: US 2004-832733 20040427 (10)
DOCUMENT TYPE: Utility

DOCUMENT TYPE: FILE SEGMENT:

FILE SEGMENT: GRANTED
PRIMARY EXAMINER: Hamilton, Cynthia
LEGAL REPRESENTATIVE: Masse, Michael A.

NUMBER OF CLAIMS: 13
EXEMPLARY CLAIM: 1,8,9,10,11
LINE COUNT: 561

LINE COUNT: 561

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

The present invention relates to photocurable compositions for use in flexographic printing plates comprising selectively hydrogenated block copolymers of conjugated

dienes and monoalkenyl arenes and flexographic printing plates

made from the same. The block copolymers, either linear or radial, have terminal blocks of unsaturated conjugated diene. The block copolymer is further comprised of monoalkenyl arene blocks and hydrogenated conjugated diene blocks. The compositions exhibit exceptional improvement in degree of cure over comparative selectively hydrogenated block copolymers.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 6 OF 9 USPAT2 on STN

2003:258532 USPAT2 ACCESSION NUMBER:

TITLE: Articles prepared from hydrogenated controlled

distribution block copolymers

Handlin, Jr., Dale Lee, Houston, TX, UNITED STATES INVENTOR(S):

Willis, Carl Lesley, Houston, TX, UNITED STATES

Clawson, Margaret Ann Burns, Houston, TX, UNITED STATES de Groot, Hendrik, Ottignies Louvain-La Neuve, BELGIUM

Eiden, Keith Edward, Houston, TX, UNITED STATES

PATENT ASSIGNEE(S): Kraton Polymers U.S. LLC, Houston, TX, UNITED STATES

(U.S. corporation)

NUMBER KIND DATE PATENT INFORMATION: US 7267855 B2 20070911 APPLICATION INFO.: US 2003-359907 20030206 (10)

RELATED APPLN. INFO.: Continuation of Ser. No. US 2002-209285, filed on 31

Jul 2002, ABANDONED

NUMBER DATE _____

US 2002-355210P 20020207 (60) PRIORITY INFORMATION:

DOCUMENT TYPE: Utility FILE SEGMENT: GRANTED PRIMARY EXAMINER: Mullis, Jeffrey

LEGAL REPRESENTATIVE: Vance, Dean F, Tackett, Keith M., Masse, Michael A.

NUMBER OF CLAIMS: 55 EXEMPLARY CLAIM: 1 LINE COUNT: 1698

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

The present invention relates to articles prepared from novel anionic

block copolymers of mono alkenyl arenes and conjugated dienes, and to blends of such block copolymers with other polymers. The block

copolymers are selectively hydrogenated and have mono alkenyl

arene end blocks and controlled distribution blocks of mono alkenyl

arenes and conjugated dienes. The block

copolymer may be blended with at least one other polymer

selected from the group consisting of olefin polymers, styrene polymers,

amorphous resins and engineering thermoplastic resins.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 7 OF 9 USPAT2 on STN

ACCESSION NUMBER: 2003:251785 USPAT2

TITLE: Adhesives and sealants from controlled distribution

block copolymers

INVENTOR(S): St. Clair, David J., Houston, TX, UNITED STATES

Handlin, Jr., Dale Lee, Houston, TX, UNITED STATES

Willis, Carl L., Houston, TX, UNITED STATES

PATENT ASSIGNEE(S): KRATON Polymers U.S. LLC, Houston, TX, UNITED STATES

(U.S. corporation)

NUMBER KIND DATE ______ PATENT INFORMATION: US 6987142 B2 20060117 APPLICATION INFO.: US 2003-359927 20030206 (10)

RELATED APPLN. INFO.: Continuation of Ser. No. US 2002-355210, filed on 7 Feb

2002, PENDING

DOCUMENT TYPE: Utility FILE SEGMENT: GRANTED
PRIMARY EXAMINER: Mullis, Jeffrey

LEGAL REPRESENTATIVE: Vance, Dean F., Masse, Michael A.

NUMBER OF CLAIMS: 36 NUMBER OF CLAIM: 1
EXEMPLARY CLAIM: 1
1056

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

The present invention relates to adhesives and sealants prepared from

novel anionic block copolymers of mono alkenyl

arenes and conjugated dienes, and to blends of such

block copolymers with other polymers. The

block copolymers are selectively hydrogenated and have

mono alkenyl arene end blocks and controlled distribution blocks of mono

alkenyl arenes and conjugated dienes. The

block copolymer may be combined with tackifying

resins, oils and other components to form the adhesives and sealants of

the present invention.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 8 OF 9 USPAT2 on STN

ACCESSION NUMBER: 2003:220390 USPAT2

TITLE: Gels from controlled distribution block copolymers INVENTOR(S): St. Clair, David J., Houston, TX, UNITED STATES Handlin, Jr., Dale Lee, Houston, TX, UNITED STATES

Willis, Carl L., Houston, TX, UNITED STATES

PATENT ASSIGNEE(S): Kraton Polymers U.S. LLC, Houston, TX, UNITED STATES

(U.S. corporation)

NUMBER KIND DATE PATENT INFORMATION: US 7141621 B2 20061128 APPLICATION INFO.: US 2003-359462 B2 20030206 20030206 (10)

> NUMBER DATE _____

PRIORITY INFORMATION: US 2002-355210P 20020207 (60)

DOCUMENT TYPE: Utility
FILE SEGMENT: GRANTED
PRIMARY EXAMINER: Mullis, Jeffrey
LEGAL REPRESENTATIVE: Vance, Dean F., Masse, Michael A.

NUMBER OF CLAIMS: 18
EXEMPLARY CLAIM: 1
LINE COUNT: 556

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

The present invention relates to gels prepared from novel anionic

block copolymers of mono alkenyl arenes and conjugated dienes, and to blends of such block copolymers with other polymers. The block

copolymers are selectively hydrogenated and have mono alkenyl

arene end blocks and controlled distribution blocks of mono alkenyl arenes and conjugated dienes. The block copolymer may be combined with tackifying resins, oils and other components to form the gels of the present invention.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L5 ANSWER 9 OF 9 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1989:622172 CAPLUS

DOCUMENT NUMBER: 111:222172

ORIGINAL REFERENCE NO.: 111:36737a,36740a

TITLE: Multilayer, sheetlike, photosensitive recording

material for printing plate production

INVENTOR(S): Kurtz, Karl Rudolf; Koch, Horst; Telser, Thomas; Bach,

Helmut

PATENT ASSIGNEE(S): BASF A.-G., Fed. Rep. Ger.

SOURCE: Ger. Offen., 20 pp.

CODEN: GWXXBX

DOCUMENT TYPE: Patent LANGUAGE: German

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PAT	PATENT NO.				D DATE	API	PLICATION NO.		DATE
DE	37369	 80		 A1	19890518	DE	 1987-3736980		19871031
EP	31661	8		A2	19890524	EP	1988-117696		19881025
EP	31661	8		АЗ	19910320				
EP	31661	8		В1	19940817				
	R: :	BE, D	E, FR,	GB,	IT, NL, SE				
JP	01154	138		A	19890616	JP	1988-273378		19881031
US	49467	58		А	19900807	US	1988-264893		19881031
US	50359	81		Α	19910730	US	1990-475802		19900206
PRIORITY	APPL	N. IN	FO.:			DE	1987-3736980	A	19871031
						US	1988-264893	А3	19881031

OTHER SOURCE(S): MARPAT 111:222172

AB Multilayer, sheetlike, photosensitive recording materials, which can be used for the production of photopolymer letterpress, intaglio, flexog., and relief printing plates, as well as photoresists, contain a relief-forming layer, which upon imagewise exposure with actinic light produces a solubility difference between the exposed and nonexposed regions so that the layer can be developed with organic, aqueous alc. or aqueous alkaline liquid media, containing

- ≥ 1 polymer binder 20-98.999, ≥ 1 photopolymn. initiator 0.001-10, ≥ 1 binder-compatible component containing a photopolymerizable olefinic group 1-60, and ≥ 1 additive that can be used to vary the characteristic profile of the material 0-40 weight%, a top layer containing $\leq 20\%$ of ≥ 1 compound selected from tertiary amines and amides and/or quaternary ammonium salts, and a strippable top foil. Thus, a PET support was overcoated with a composition containing an isoprene-styrene block copolymer,
- 1,6-hexanediol diacrylate, benzil di-E acetal, a chloro paraffin , an α methylstyrene-p-methylstyrene oligomer,
- 2,6-di-tert-butyl-p-cresol, and solvent Black 3 to give a relief-forming layer, a top layer containing an ethylene-propylene rubber, and N,N-bis(2-hydroxyethyl)-N-stearylamine, and a matte PET top foil. Upon exposure and development of this material, a flexog. plate having a low electrostatic charge and capable of producing a high number of prints was obtained.

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ANSWER 8 OF 9 USPAT2 on STN L5

ACCESSION NUMBER: 2003:220390 USPAT2

Gels from controlled distribution block copolymers TITLE: INVENTOR(S): St. Clair, David J., Houston, TX, UNITED STATES

Handlin, Jr., Dale Lee, Houston, TX, UNITED STATES

Willis, Carl L., Houston, TX, UNITED STATES

PATENT ASSIGNEE(S): Kraton Polymers U.S. LLC, Houston, TX, UNITED STATES

(U.S. corporation)

NUMBER KIND DATE _____ PATENT INFORMATION: US 7141621 B2 20061128 US 2003-359462 20030206 20030206 (10) APPLICATION INFO.:

> NUMBER DATE _____

US 2002-355210P 20020207 (60) PRIORITY INFORMATION:

DOCUMENT TYPE: Utility PRIMARY EXAMINER:
LEGAL REPRESENT GRANTED

Mullis, Jeffrey

LEGAL REPRESENTATIVE: Vance, Dean F., Masse, Michael A. NUMBER OF CLAIMS: 18

NUMBER OF CLAIMS: EXEMPLARY CLAIM: 1 556 LINE COUNT:

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

The present invention relates to gels prepared from novel anionic block copolymers of mono alkenyl arenes and conjugated dienes, and to blends of such block copolymers with other polymers. The block copolymers are selectively hydrogenated and have mono alkenyl arene end blocks and controlled distribution blocks of mono alkenyl arenes and conjugated dienes. The block copolymer may be combined with tackifying resins, oils and other

components to form the gels of the present invention. PARN The present application is related to copending, commonly assigned U.S.

patent application Ser. No. 10/359,981 entitled Novel Block Copolymers and Method for Making Same, now published as US2003/0176582 A1, commonly assigned U.S. patent application Ser. No. 10/359,906 entitled Polymer Modified Bitumen Compositions, now U.S. Pat. No. 6,759,454, copending, commonly assigned U.S. patent application Ser. No. 10/359,953 entitled Articles Prepared from Controlled Distribution Block Copolymers, now published as US2003/0166776 A1, copending, commonly assigned U.S. patent application Ser. No. 10/359,907 entitled Articles Prepared From Hydrogenated Controlled Distribution

Block Copolymers, now published as US2003/0181585 A1, copending, commonly assigned U.S. patent application Ser. No. 10/359,927 entitled Adhesives and Sealants From Controlled Distribution

Block Copolymers, now published as US2003/0176574 A1,

all of which were filed Feb. 6, 2003 and copending, commonly assigned International Patent Application Serial Number PCT/NL03/00098 filed on Feb. 7, 2003 entitled Solvent-Free, Hot Melt Adhesive Composition Comprising a Controlled Distribution Block Copolymer

, now published as WO 03/066769 A1, and copending, commonly assigned U.S. patent application Ser. No. 10/745,352 filed Dec. 12, 2003, entitled Gels from Controlled Distribution Block

Copolymers, now published as US2004/0138371 A1, which is a continuation-in-part of U.S. patent application Ser. No. 10/359,462, and copending, commonly assigned U.S. patent application Ser. No. 10/681,608 filed Oct. 8, 2003 entitled Photopolymerizable Compositions and Flexographic Printing Plates Prepared from Controlled Distribution Block Copolymers, now published as US2004/0072951, all of which claim the benefit of U.S. Provisional Patent Application Ser. No. 60/355,210 filed Feb. 7, 2002.

SUMM This invention relates to gels prepared from novel anionic block copolymers of mono alkenyl arenes and conjugated dienes.

SUMM The preparation of block copolymers of mono alkenyl arenes and conjugated dienes is well known. One of the first patents on linear ABA block copolymers made with styrene and butadiene is U.S. Pat. No. 3,149,182. These polymers in turn could be hydrogenated to form more stable block copolymers, such as those described in U.S. Pat. No. 3,595,942 and U.S. Pat. No. Re. 27,145. Such polymers are broadly termed Styrenic Block Copolymers or SBC's.

Now a novel anionic block copolymer based on mono alkenyl arene end blocks and controlled distribution mid blocks of mono alkenyl arenes and conjugated dienes has been discovered and is described in copending, commonly assigned U.S. patent application Ser. No. 60/355,210, entitled "NOVEL BLOCK COPOLYMERS AND METHOD FOR MAKING SAME". Methods for making such polymers are described in detail in the above-mentioned patent application. Patentees have found that these new polymers will allow the preparation of improved oil gels. In particular, this invention comprises a new class of SBC's in which the polymer manufacturer can vary the compatibility characteristics of the rubber segment, resulting in improved oil gels.

SUMM In one aspect of the present invention we have discovered a novel oil gel composition comprising 100 parts by weight of at least one hydrogenated block copolymer having a controlled distribution block of a mono alkenyl arene and conjugated diene and 350 to 2000 parts by weight of an extender oil. The hydrogenated block copolymer has at least one polymer block A and at least one polymer block B wherein (a.) prior to hydrogenation each A block is a mono alkenyl arene homopolymer block and each B block is a controlled distribution copolymer block of at least one conjugated diene and at least one mono alkenyl arene; (b.) subsequent to hydrogenation about 0-10% of the arene double bonds have been reduced, and at least about 90% of the conjugated diene double bonds have been reduced; (c.) each A block having a number average molecular weight between about 3,000 and about 60,000 and each B block having a number average molecular weight between about 30,000 and about 300,000; (d.) each B block comprises terminal regions adjacent to the A blocks that are rich in conjugated diene units and one or more regions not adjacent to the A blocks that are rich in mono alkenyl arene units; (e.) the total amount of mono alkenyl arene in the hydrogenated block copolymer is about 20 percent weight to about 80 percent weight; and (f.) the weight percent of mono alkenyl arene in each B block is between about 10 percent and about 75 percent. The general configuration of the block copolymer is A-B, A-B-A, (A-B).sub.n, (A-B).sub.n-A, (A-B-A).sub.nX, (A-B).sub.nX or a mixture thereof, where n is an integer from 2 to about 30, preferably 2 to about 15, more preferably 2 to about 6, and X is coupling agent

residue.

DETD The key component of the present invention is the novel block copolymer containing mono alkenyl arene end blocks and a unique mid block of a mono alkenyl arene and a conjugated diene. Surprisingly, the combination of (1) a unique control for the monomer addition and (2) the use of diethyl ether or other modifiers as a component of the solvent (which will be referred to as "distribution agents") results in a certain characteristic distribution of the two monomers (herein termed a "controlled distribution" polymerization, i.e., a polymerization resulting in a "controlled distribution" structure), and also results in the presence of certain mono alkenyl arene rich regions and certain conjugated diene rich regions in the polymer block. For purposes hereof, "controlled distribution" is defined as referring to a molecular structure having the following attributes: (1) terminal regions adjacent to the mono alkenyl arene homopolymer ("A") blocks that are rich in (i.e., having a greater than average amount of) conjugated diene units; (2) one or more regions not adjacent to the A blocks that are rich in (i.e., having a greater than average number of) mono alkenyl arene units; and (3) an overall structure having relatively low blockiness. For the purposes hereof, "rich in" is defined as greater than the average amount, preferably greater than 5% of the average amount. This relatively low blockiness can be shown by either the presence of only a single glass transition temperature (Tg) intermediate between the Tg's of either monomer alone, when analyzed using differential scanning calorimetry ("DSC") thermal methods or via mechanical methods, or as shown via proton nuclear magnetic resonance ("H-NMR") methods. The potential for blockiness can also be inferred from measurement of the UV-visible absorbance in a wavelength range suitable for the detection of polystyryllithium end groups during the polymerization of the B block. A sharp and substantial increase in this value is indicative of a substantial increase in polystyryllithium chain ends. In this process, this will only occur if the conjugated diene concentration drops below the critical level to maintain controlled distribution polymerization. Any styrene monomer that is present at this point will add in a blocky fashion. The term "styrene blockiness", as measured by those skilled in the art using proton NMR, is defined to be the proportion of S units in the polymer having two S nearest neighbors on the polymer chain. The styrene blockiness is determined after using H-1 NMR to measure two experimental quantities as follows:

DETD In a preferred embodiment of the present invention, the subject controlled distribution copolymer block has two distinct types of regions—conjugated diene rich regions on the ends of the block and a mono alkenyl arene rich region near the middle or center of the block. What is desired is a mono alkenyl arene/conjugated diene controlled distribution copolymer block, wherein the proportion of mono alkenyl arene units increases gradually to a maximum near the middle or center of the block and then decreases gradually until the polymer block is fully polymerized. This structure is distinct and different from the tapered and/or random structures discussed in the prior art.

DETD It is also important to control the molecular weight of the various blocks. For an AB diblock, desired block weights are 3,000 to about 60,000 for the mono alkenyl arene A block, and 30,000 to about 300,000 for the controlled distribution conjugated diene /mono alkenyl arene B block. Preferred ranges are 5000 to 45,000 for the A block and 50,000 to about 250,000 for the B block. For the triblock,

which may be a sequential ABA or coupled (AB).sub.2 X block copolymer, the A blocks should be 3,000 to about 60,000, preferably 5000 to about 45,000, while the B block for the sequential block should be about 30,000 to about 300,000, and the B blocks (two) for the coupled polymer half that amount. The total average molecular weight for the triblock copolymer should be from about 40,000 to about 400,000, and for the radial copolymer from about 60,000 to about 600,000. These molecular weights are most accurately determined by light scattering measurements, and are expressed as number average molecular weights.

- DETD Another important aspect of the present invention is to control the microstructure or vinyl content of the conjugated diene in the controlled distribution copolymer block. The term "vinyl content" refers to a conjugated diene which is polymerized via 1,2-addition (in the case of butadiene -- it would be 3,4-addition in the case of isoprene). Although a pure "vinyl" group is formed only in the case of 1,2-addition polymerization of 1,3butadiene, the effects of 3,4-addition polymerization of isoprene (and similar addition for other conjugated dienes) on the final properties of the block copolymer will be similar. The term "vinyl" refers to the presence of a pendant vinyl group on the polymer chain. When referring to the use of butadiene as the conjugated diene, it is preferred that about 20 to about 80 mol percent of the condensed butadiene units in the copolymer block have 1,2 vinyl configuration as determined by proton NMR analysis, preferably about 30 to about 70 mol percent of the condensed butadiene units should have 1,2-vinyl configuration. This is effectively controlled by varying the relative amount of the distribution agent. As will be appreciated, the distribution agent serves two purposes -- it creates the controlled distribution of the mono alkenyl arene and conjugated diene, and also controls the microstructure of the conjugated diene. Suitable ratios of distribution agent to lithium are disclosed and taught in U.S. Pat. No. Re. 27,145, which disclosure is incorporated by reference.
- DETD The block copolymer is selectively hydrogenated. Hydrogenation can be carried out via any of the several hydrogenation or selective hydrogenation processes known in the prior art. For example, such hydrogenation has been accomplished using methods such as those taught in, for example, U.S. Pat. Nos. 3,494,942; 3,634,594; 3,670,054; 3,700,633; and U.S. Pat. No. Re. 27,145. Hydrogenation can be carried out under such conditions that at least about 90 percent of the conjugated diene double bonds have been reduced, and between zero and 10 percent of the arene double bonds have been reduced. Preferred ranges are at least about 95 percent of the conjugated diene double bonds reduced, and more preferably about 98 percent of the conjugated diene double bonds are reduced. Alternatively, it is possible to hydrogenate the polymer such that aromatic unsaturation is also reduced beyond the 10 percent level mentioned above. In that case, the double bonds of both the conjugated diene and arene may be reduced by 90 percent or more.
- DETD In an alternative, the block copolymer of the present invention may be functionalized in a number of ways. One way is by treatment with an unsaturated monomer having one or more functional groups or their derivatives, such as carboxylic acid groups and their salts, anhydrides, esters, imide groups, amide groups, and acid chlorides. The preferred monomers to be grafted onto the block

copolymers are maleic anhydride, maleic acid, fumaric acid, and their derivatives. A further description of functionalizing such block copolymers can be found in Gergen et al, U.S. Pat. Nos. 4,578,429 and in 5,506,299. In another manner the selectively hydrogenated block copolymer of the present invention may be functionalized by grafting silicon or boron containing compounds to the polymer as taught in U.S. Pat. No. 4,882,384. In still another manner, the block copolymer of the present invention may be contacted with an alkoxy-silane compound to form silane-modified block copolymer. In yet another manner, the block copolymer of the present invention may be functionalized by reacting at least one ethylene oxide molecule to the polymer as taught in U.S. Pat. No. 4,898,914, or by reacting the polymer with carbon dioxide as taught in U.S. Pat. No. 4,970,265. Still further, the block copolymers of the present invention may be metallated as taught in U.S. Pat. Nos. 5,206,300 and 5,276,101, wherein the polymer is contacted with an alkali metal alkyl, such as a lithium alkyl. And still further, the block copolymers of the present invention may be functionalized by grafting sulfonic groups to the polymer as taught in U.S. Pat. No. 5,516,831.

Controlled distribution block copolymers of the DETD present invention were prepared according to the process disclosed in copending patent application Ser. No. 60/355,210 referenced above, including it's continuing application filed concurrently. The polymers were selectively hydrogenated ABA block copolymers where the A blocks were polystyrene blocks and the B block prior to hydrogenation was a styrene butadiene controlled distribution block having terminal regions that are rich in butadiene units and a center region that was rich in styrene units. The polymers are shown in Table 1 below. Step I MW is the molecular weight of the first A block, Step II MW is the molecular weight of the AB blocks and Step III MW is the molecular weight of the ABA blocks. The polymers were hydrogenated such that greater than about 95% of the diene double bonds have been reduced. What is claimed is:

CLM

1. An oil gel composition comprising 100 parts by weight of at least one hydrogenated block copolymer and from about 400 to about 2000 parts by weight of an extending oil, wherein said hydrogenated block copolymer has at least one polymer block A and at least one polymer block B, and wherein: a. prior to hydrogenation each A block is a mono alkenyl arene homopolymer block and each B block is a controlled distribution copolymer block of at least one conjugated diene and at least one mono alkenyl arene; b. subsequent to hydrogenation about 0-10% of the arene double bonds have been reduced, and at least about 90% of the conjugated diene double bonds have been reduced; c. each A block having a number average molecular weight between about 3,000 and about 60,000 and each B block having a number average molecular weight between about 20,000 and about 300,000; d. each B block comprises terminal regions adjacent to the A blocks that are rich in conjugated diene units and one or more regions not adjacent to the A blocks that are rich in mono alkenyl arene units; e. the total amount of mono alkenyl arene in the hydrogenated block copolymer is about 20 percent weight to about 80 percent weight; and f. the weight percent of mono alkenyl arene in each B block is between about 10 percent and about 75 percent.

5. The oil gel composition according to claim 4 wherein the polymer is an ABA polymer and each block B has a center region with a minimum ratio of butadiene units to styrene units.

CLM What is claimed is:

> 8. The oil gel composition according to claim 7 wherein said hydrogenated block copolymer is a linear hydrogenated ABA styrene/butadiene block copolymer having a total number average molecular weight of about 80,000 to about 140,000.

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ANSWER 7 OF 9 USPAT2 on STN

ACCESSION NUMBER: 2003:251785 USPAT2

Adhesives and sealants from controlled distribution TITLE:

block copolymers

INVENTOR(S): St. Clair, David J., Houston, TX, UNITED STATES

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KRATON Polymers U.S. LLC, Houston, TX, UNITED STATES PATENT ASSIGNEE(S):

(U.S. corporation)

NUMBER KIND DATE ______ PATENT INFORMATION: US 6987142 B2 20060117 US 2003-359927 20030206 (10)

RELATED APPLN. INFO.:

Continuation of Ser. No. US 2002-355210, filed on 7 Feb

2002, PENDING

DOCUMENT TYPE: Utility FILE SEGMENT: GRANTED

PRIMARY EXAMINER: Mullis, Jeffrey

LEGAL REPRESENTATIVE: Vance, Dean F., Masse, Michael A.

NUMBER OF CLAIMS: 36 EXEMPLARY CLAIM: 1 LINE COUNT: 1056

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

The present invention relates to adhesives and sealants prepared from novel anionic block copolymers of mono alkenyl

arenes and conjugated dienes, and to blends of such

block copolymers with other polymers. The

block copolymers are selectively hydrogenated and have

mono alkenyl arene end blocks and controlled distribution blocks of mono

alkenyl arenes and conjugated dienes. The

block copolymer may be combined with tackifying

resins, oils and other components to form the adhesives and sealants of the present invention.

The present application is related to, commonly assigned U.S. patent PARN application Ser. No. 10/359,981 entitled Novel Block Copolymers and Method for Making Same, now published as US2003/0176582 A1, commonly assigned U.S. patent application Ser. No. 10/359,906 entitled Polymer Modified Bitumen Compositions, now U.S. Pat. No. 6,759,454, commonly assigned U.S. patent application Ser. No. 10/359,953 entitled Articles Prepared from Controlled Distribution

Block Copolymers, now published as US2003/0166776 A1, commonly assigned U.S. patent application Ser. No. 10/359,907 entitled

Articles Prepared From Hydrogenated Controlled Distribution

Block Copolymers, now published as US2003/0181585 A1,

commonly assigned U.S. patent application Ser. No. 10/359,462 entitled Gels From Controlled Distribution Block Copolymers, now published as US2003/0153681 A1, all of which were filed Feb. 6, 2003 and commonly assigned International Patent Application Ser. No. PCT/NL03/00098 filed on Feb. 7, 2003 entitled Solvent-Free, Hot Melt Adhesive Composition Comprising a Controlled Distribution Block Copolymer, now published as WO 03/066769 A1, and, commonly assigned U.S. patent application Ser. No. 10/745,352 filed Dec. 12, 2003, entitled Gels from Controlled Distribution Black Copolymers, now published as US2004/0138371 A1, which is a continuation-in-part of U.S. patent application Ser. No. 10/359,462, and, commonly assigned U.S. patent application Ser. No. 10/681,608 filed Oct. 8, 2003 entitled Photopolymerizable Compositions and Flexographic Printing Plates Prepared from Controlled Distribution Block Copolymers , now published as US2004/0072951, all of which claim the benefit of U.S. Provisional Patent Application Ser. No. 60/355,210 filed Feb. 7, 2002.

- SUMM This invention relates to adhesives and sealants prepared from novel anionic block copolymers of mono alkenyl arenes and conjugated dienes.
- SUMM The preparation of block copolymers of mono alkenyl arenes and conjugated dienes is well known. One of the first patents on linear ABA block copolymers made with styrene and butadiene is U.S. Pat. No. 3,149,182. These polymers in turn could be hydrogenated to form more stable block copolymers, such as those described in U.S. Pat. No. 3,595,942 and U.S. Pat. No. Re. 27,145. Such polymers are broadly termed Styrenic Block Copolymers or SBC's.
- SUMM SBC's have a long history of use as adhesives and sealants. For example, U.S. Pat. No. 3,239,478 ("Harlan") discloses adhesives comprising unsaturated styrene-isoprene-styrene block copolymers ("SIS") and styrene-butadiene-styrene block copolymers ("SBS") in adhesives and sealants. Harlan also broadly discloses adhesives comprising the hydrogenated S-B-S (i.e. "SEBS") and hydrogenated S-I-S (i.e. "SEPS") block copolymers with tackifying resins and extender oils for a variety of adhesives and sealants, including pressure sensitive adhesives. It is known in the art that resins which are compatible with the rubber segment of the SBC's are responsible for development of tack in pressure sensitive adhesives. Heretofore, it has not been possible to prepare SBC's in which the compatibility characteristics of the rubber segment could be controlled by the polymer manufacturer. Therefore, much work has been done by resin manufacturers to develop new resins tailored for optimum compatibility with each of the different types of SBC. For example, aliphatic resins have good compatibility with SIS and SEBS (i.e. hydrogenated SBS polymers) type SBC's but not with SBS type. New aliphatic/aromatic resins have been developed which have good compatibility with SBS type SBC's. This invention comprises a new class of SBC's in which the polymer manufacturer can vary the compatibility characteristics of the rubber segment.
- SUMM Now a novel anionic block copolymer based on mono alkenyl arene end blocks and controlled distribution mid blocks of mono alkenyl arenes and conjugated dienes has been discovered and is described in copending, commonly assigned U.S. patent application Ser. No. 60/355,210, entitled "NOVEL BLOCK COPOLYMERS AND METHOD FOR MAKING SAME". Methods for making such polymers are described in detail in the above-mentioned patent

application. Patentees have found that the resin compatibility of these new polymers is indeed different from conventional hydrogenated SBC's which will allow resin manufacturers the opportunity to develop new resins which are compatible with these novel SBC's. Patentees have also found that phase stable, clear adhesives can be made using blends of unsaturated SBC's, especially certain SIS polymers, with these new polymers. This allows formulators to develop hot melt PSA's which have the good melt stability found for hydrogenated SBC's but better tack.

In one aspect of the present invention we have discovered a novel adhesive composition comprising 100 parts by weight of at least one hydrogenated block copolymer having a controlled distribution block of a mono alkenyl arene and conjugated diene, 25 to 300 parts by weight of at least one tackifying resin, and 0 to 200 parts by weight of an extender oil. The hydrogenated block copolymer has at least one polymer block A and at least one polymer block B wherein (a.) prior to hydrogenation each A block is a mono alkenyl arene homopolymer block and each B block is a controlled distribution copolymer block of at least one conjugated diene and at least one mono alkenyl arene; (b.) subsequent to hydrogenation about 0-10 % of the arene double bonds have been reduced, and at least about 90% of the conjugated diene double bonds have been reduced; (c.) each A block having a number average molecular weight between about 3,000 and about 60,000 and each B block having a number average molecular weight between about 30,000 and about 300,000; (d.) each B block comprises terminal regions adjacent to the A blocks that are rich in conjugated diene units and one or more regions not adjacent to the A blocks that are rich in mono alkenyl arene units; (e.) the total amount of mono alkenyl arene in the hydrogenated block copolymer is about 20 percent weight to about 80 percent weight; and (f.) the weight percent of mono alkenyl arene in each B block is between about 10 percent and about 75 percent. The general configuration of the block copolymer is A-B, A-B-A, (A-B).sub.n, (A-B).sub.n-A, (A-B-A).sub.nX or (A-B).sub.nX; where n is an integer from 2 to about 30, preferably 2 to about 15, more preferably 2 to about 6, and X is coupling agent residue. The adhesive compositions of the present invention include hot melt adhesives, pressure sensitive adhesives, solvent-based adhesives, and the like.

In another aspect of the present invention we have shown that a clear, phase stable adhesive composition can be prepared with the controlled distribution block copolymers in blends with certain SIS type SBC's. This adhesive composition comprises 100 parts by weight of the controlled distribution block copolymer, about 25 to about 300 parts by weight of a styrene/isoprene unhydrogenated block copolymer, about 50 to about 400 parts by weight of a tackifying resin, and about 0 to about 200 parts by weight of a polymer extending oil. The novel polymers can be added to an adhesive based on an SIS polymer to improve stability or an SIS polymer can be included in an adhesive based on the novel polymer to improve tack.

DETD The key component of the present invention is the novel block copolymer containing mono alkenyl arene end blocks and a unique mid block of a mono alkenyl arene and a conjugated diene. Surprisingly, the combination of (1) a unique control for the monomer addition and (2) the use of diethyl ether or other modifiers as a component of the solvent (which will be referred to as

"distribution agents") results in a certain characteristic distribution of the two monomers (herein termed a "controlled distribution" polymerization, i.e., a polymerization resulting in a "controlled distribution" structure), and also results in the presence of certain mono alkenyl arene rich regions and certain conjugated diene rich regions in the polymer block. For purposes hereof, "controlled distribution" is defined as referring to a molecular structure having the following attributes: (1) terminal regions adjacent to the mono alkenyl arene homopolymer ("A") blocks that are rich in (i.e., having a greater than average amount of) conjugated diene units; (2) one or more regions not adjacent to the A blocks that are rich in (i.e., having a greater than average number of) mono alkenyl arene units; and (3) an overall structure having relatively low blockiness. For the purposes hereof, "rich in" is defined as greater than the average amount, preferably greater than 5% of the average amount. This relatively low blockiness can be shown by either the presence of only a single glass transition temperature (Tg) intermediate between the Tg's of either monomer alone, when analyzed using differential scanning calorimetry ("DSC") thermal methods or via mechanical methods, or as shown via proton nuclear magnetic resonance ("H-NMR") methods. The potential for blockiness can also be inferred from measurement of the UV-visible absorbance in a wavelength range suitable for the detection of polystyryllithium end groups during the polymerization of the B block. A sharp and substantial increase in this value is indicative of a substantial increase in polystyryllithium chain ends. In this process, this will only occur if the conjugated diene concentration drops below the critical level to maintain controlled distribution polymerization. Any styrene monomer that is present at this point will add in a blocky fashion. The term "styrene blockiness", as measured by those skilled in the art using proton NMR, is defined to be the proportion of S units in the polymer having two S nearest neighbors on the polymer chain. The styrene blockiness is determined after using H-1 NMR to measure two experimental quantities as follows:

- DETD In a preferred embodiment of the present invention, the subject controlled distribution copolymer block has two distinct types of regions—conjugated diene rich regions on the ends of the block and a mono alkenyl arene rich region near the middle or center of the block. What is desired is a mono alkenyl arene/conjugated diene controlled distribution copolymer block, wherein the proportion of mono alkenyl arene units increases gradually to a maximum near the middle or center of the block and then decreases gradually until the polymer block is fully polymerized. This structure is distinct and different from the tapered and/or random structures discussed in the prior art.
- DETD It is also important to control the molecular weight of the various blocks. For an AB diblock, desired block weights are 3,000 to about 60,000 for the mono alkenyl arene A block, and 30,000 to about 300,000 for the controlled distribution conjugated diene /mono alkenyl arene B block. Preferred ranges are 5000 to 45,000 for the A block and 50,000 to about 250,000 for the B block. For the triblock, which may be a sequential ABA or coupled (AB).sub.2 X block copolymer, the A blocks should be 3,000 to about 60,000, preferably 5000 to about 45,000, while the B block for the sequential block should be about 30,000 to about 300,000, and the B blocks (two) for the coupled polymer half that amount. The total average molecular weight for the triblock copolymer should be from about 40,000 to about 400,000, and for the radial copolymer from about 60,000 to about 600,000. These molecular weights are most

accurately determined by light scattering measurements, and are expressed as number average molecular weights.

DETD Another important aspect of the present invention is to control the microstructure or vinyl content of the conjugated diene in the controlled distribution copolymer block. The term "vinyl content" refers to a conjugated diene which is polymerized via 1,2-addition (in the case of butadiene--it would be 3,4-addition in the case of isoprene). Although a pure "vinyl" group is formed only in the case of 1,2-addition polymerization of 1,3butadiene, the effects of 3,4-addition polymerization of isoprene (and similar addition for other conjugated dienes) on the final properties of the block copolymer will be similar. The term "vinyl" refers to the presence of a pendant vinyl group on the polymer chain. When referring to the use of butadiene as the conjugated diene, it is preferred that about 20 to about 80 mol percent of the condensed butadiene units in the copolymer block have 1,2 vinyl configuration as determined by proton NMR analysis, preferably about 30 to about 70 mol percent of the condensed butadiene units should have 1,2-vinyl configuration. This is effectively controlled by varying the relative amount of the distribution agent. As will be appreciated, the distribution agent serves two purposes -- it creates the controlled distribution of the mono alkenyl arene and conjugated diene, and also controls the microstructure of the conjugated diene. Suitable ratios of distribution agent to lithium are disclosed and taught in U.S. Pat. No. Re 27,145, which disclosure is incorporated by reference.

The block copolymer is selectively hydrogenated. DETD Hydrogenation can be carried out via any of the several hydrogenation or selective hydrogenation processes known in the prior art. For example, such hydrogenation has been accomplished using methods such as those taught in, for example, U.S. Pat. Nos. 3,494,942; 3,634,594; 3,670,054; 3,700,633; and Re. 27,145. Hydrogenation can be carried out under such conditions that at least about 90 percent of the conjugated diene double bonds have been reduced, and between zero and 10 percent of the arene double bonds have been reduced. Preferred ranges are at least about 95 percent of the conjugated diene double bonds reduced, and more preferably about 98 percent of the conjugated diene double bonds are reduced. Alternatively, it is possible to hydrogenate the polymer such that aromatic unsaturation is also reduced beyond the 10 percent level mentioned above. In that case, the double bonds of both the conjugated diene and arene may be reduced by 90 percent or more.

DETD In an alternative, the block copolymer of the present invention may be functionalized in a number of ways. One way is by treatment with an unsaturated monomer having one or more functional groups or their derivatives, such as carboxylic acid groups and their salts, anhydrides, esters, imide groups, amide groups, and acid chlorides. The preferred monomers to be grafted onto the block copolymers are maleic anhydride, maleic acid, fumaric acid, and their derivatives. A further description of functionalizing such block copolymers can be found in Gergen et al, U.S. Pat. No. 4,578,429 and in U.S. Pat. No. 5,506,299. In another manner the selectively hydrogenated block copolymer of the present invention may be functionalized by grafting silicon or boron containing compounds to the polymer as taught in U.S. Pat. No. 4,882,384. In still another manner, the block

copolymer of the present invention may be contacted with an alkoxy-silane compound to form silane-modified block copolymer. In yet another manner, the block copolymer of the present invention may be functionalized by reacting at least one ethylene oxide molecule to the polymer as taught in U.S. Pat. No. 4,898,914, or by reacting the polymer with carbon dioxide as taught in U.S. Pat. No. 4,970,265. Still further, the block copolymers of the present invention may be metallated as taught in U.S. Pat. Nos. 5,206,300 and 5,276,101, wherein the polymer is contacted with an alkali metal alkyl, such as a lithium alkyl. And still further, the block copolymers of the present invention may be functionalized by grafting sulfonic groups to the polymer as taught in U.S. Pat. No. 5,516,831.

DETD TABLE A

Applications, Compositions and Ranges

		Composition,
Application	Ingredients	Parts by weight
Adhesive	CD Polymer	100
	Tackifying Resin	25 to 300
	Extending Oil	0 to 200
Hot melt adhesive	CD Polymer	100
(preferred range)	Tackifying Resin	75 to 200
	End Block Resin	0 to 50
	Extending Oil	0 to 150
Solvent based adhesive	CD Polymer	100
(not including solvent)	Tackifying Resin	25 to 300
	Oil	0 to 100
Pressure sensitive adhesive	CD Polymer	100
	Styrene/Isoprene	25 to 300
	Block Copolymer	
	Tackifying Resin	50 to 500
	Oil	0 to 200
Construction adhesive or	CD Polymer	100
sealant	Tackifying Resin	0 to 200
	Endblock Resin	0 to 200
	Calcium Carbonate	100 to 800
DETD Various controlled dis	tribution block copoly	more of

DETD Various controlled distribution block copolymers of the present invention were prepared according to the process disclosed in copending patent application Serial No. 60/355,210 referenced above, including it's continuing application filed concurrently. All polymers were selectively hydrogenated AB or ABA block copolymers where the A blocks were polystyrene blocks and the B block prior to hydrogenation was a styrene butadiene controlled distribution block having terminal regions that are rich in butadiene units and a center region that was rich in styrene units. The various polymers are shown in Table 1 below. These polymers were then used in the various applications described in the other Examples. Step I MW is the molecular weight of the first A block, Step II MW is the molecular weight of the AB blocks and Step III MW is the molecular weight of the ABA blocks. The polymers were hydrogenated such that greater than about 95% of the diene double bonds have been reduced.

CLM What is claimed is:

1. A pressure sensitive adhesive composition comprising 100 parts by weight of at least one hydrogenated block copolymer, about 25 to about 300 parts by weight of a compatible styrene/

isoprene unhydrogenated block copolymer, about 25 to about 300 parts by weight of at least one tackifying resin and about zero to about 200 parts by weight of an extending oil, wherein said hydrogenated block copolymer has at least one polymer block A and at least one polymer block B, and wherein: a. prior to hydrogenation each A block is a mono alkenyl arene homopolymer block and each B block is a controlled distribution copolymer block of at least one conjugated diene and at least one mono alkenyl arene; b. subsequent to hydrogenation about 0-10% of the arene double bonds have been reduced, and at least about 90% of the conjugated diene double bonds have been reduced; c. each A block having a number average molecular weight between about 3,000 and about 60,000 and each B block having a number average molecular weight between about 20,000 and about 300,000; d. each B block comprises terminal regions adjacent to the A blocks that are rich in conjugated diene units and one or more regions not adjacent to the A blocks that are rich in mono alkenyl arene units; e. the total amount of mono alkenyl arene in the hydrogenated block copolymer is about 20 percent weight to about 80 percent weight; and f. the weight percent of mono alkenyl arene in each B block is between about 10 percent and about 75 percent.

CLM What is claimed is:

5. The adhesive composition according to claim 4 wherein the polymer is an ABA polymer and each block B has a center region with a minimum ratio of butadiene units to styrene units.

CLM What is claimed is:

18. A pressure sensitive adhesive composition comprising 100 parts by weight of at least one hydrogenated block copolymer, about 25 to about 300 parts by weight of a compatible styrene/ isoprene unhydrogenated block copolymer, about 50 to about 500 parts by weight of a tackifying resin, and about 0 to about 200 parts by weight of a polymer extending oil, wherein said hydrogenated block copolymer has the general configuration A-B, A-B-A, (A-B).sub.n (A-B).sub.n-A (A-B-A).sub.nX (A-B).sub.nX, where n is an integer from 2 to about 30, and X is coupling agent residue and wherein: a. prior to hydrogenation each A block is a mono alkenyl arene homopolymer block and each B block is a controlled distribution copolymer block of at least one conjugated diene and at least one mono alkenyl arene; b. subsequent to hydrogenation about 0-10% of the arene double bonds have been reduced, and at least about 90% of the conjugated diene double bonds have been reduced; c. each A block having a number average molecular weight between about 3,000 and about 60,000 and each B block having a number average molecular weight between about 20,000 and about 300,000; d. each B block comprises terminal regions adjacent to the A blocks that are rich in conjugated diene units and one or more regions not adjacent to the A blocks that are rich in mono alkenyl arene units; e. the total amount of mono alkenyl arene in the hydrogenated block copolymer is about 20 percent weight to about 80 percent weight; and f. the weight percent of mono alkenyl arene in each B block is between about 10 percent and about 75 percent.

CLM What is claimed is:

19. The adhesive composition according to claim 18 wherein said compatible styrene/isoprene unhydrogenated block copolymer is an S-I-S block copolymer having

a number average molecular weight of about 100,000 to about 350,000, and a styrene content of between about 12 and about 20 weight percent.

CLM What is claimed is:

> 20. The adhesive composition according to claim 19 wherein said hydrogenated block copolymer is a linear hydrogenated styrene/butadiene block copolymer having a total number average molecular weight of about 25,000 to about 150,000.

What is claimed is: CLM

> 21. The adhesive composition according to claim 20 wherein the amount of styrene/isoprene unhydrogenated block copolymer is between about 50 and about 200 parts by weight.

CLMWhat is claimed is:

22. The adhesive composition according to claim 18 wherein said styrene/ isoprene unhydrogenated block copolymer comprises a linear S-I-S block copolymer and an S-I diblock copolymer.

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L8 NOT FOUND

The L-number entered has not been defined in this session, or it has been deleted. To see the L-numbers currently defined in this session, enter DISPLAY HISTORY at an arrow prompt (=>).

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L5 ANSWER 8 OF 9 USPAT2 on STN

ACCESSION NUMBER: 2003:220390 USPAT2

TITLE: Gels from controlled distribution block copolymers St. Clair, David J., Houston, TX, UNITED STATES INVENTOR(S): Handlin, Jr., Dale Lee, Houston, TX, UNITED STATES

Willis, Carl L., Houston, TX, UNITED STATES

PATENT ASSIGNEE(S): Kraton Polymers U.S. LLC, Houston, TX, UNITED STATES

(U.S. corporation)

NUMBER KIND DATE PATENT INFORMATION: US 7141621 B2 20061128 APPLICATION INFO.: US 2003-359462 20030206 (10)

NUMBER DATE

US 2002-355210P 20020207 (60) PRIORITY INFORMATION:

DOCUMENT TYPE: Utility

FILE SEGMENT:

PRIMARY EXAMINER:

LEGAL REPRESENTATIVE:

WIMPER OF CLAIMS:

MULLIS, Jeffrey

Vance, Dean F., Masse, Michael A.

18 EXEMPLARY CLAIM: 1 LINE COUNT: 556

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

The present invention relates to gels prepared from novel anionic block copolymers of mono alkenyl arenes and conjugated dienes, and to blends of such block copolymers with other polymers. The block

copolymers are selectively hydrogenated and have mono alkenyl arene end blocks and controlled distribution blocks of mono alkenyl arenes and conjugated dienes. The block copolymer may be combined with tackifying resins, oils and other components to form the gels of the present invention.

PARN The present application is related to copending, commonly assigned U.S. patent application Ser. No. 10/359,981 entitled Novel Block Copolymers and Method for Making Same, now published as US2003/0176582 A1, commonly assigned U.S. patent application Ser. No. 10/359,906 entitled Polymer Modified Bitumen Compositions, now U.S. Pat. No. 6,759,454, copending, commonly assigned U.S. patent application Ser. No. 10/359,953 entitled Articles Prepared from Controlled Distribution Block Copolymers, now published as US2003/0166776 A1, copending, commonly assigned U.S. patent application Ser. No. 10/359,907 entitled Articles Prepared From Hydrogenated Controlled Distribution Block Copolymers, now published as US2003/0181585 A1, copending, commonly assigned U.S. patent application Ser. No. 10/359,927 entitled Adhesives and Sealants From Controlled Distribution Block Copolymers, now published as US2003/0176574 A1, all of which were filed Feb. 6, 2003 and copending, commonly assigned International Patent Application Serial Number PCT/NL03/00098 filed on Feb. 7, 2003 entitled Solvent-Free, Hot Melt Adhesive Composition Comprising a Controlled Distribution Block Copolymer , now published as WO 03/066769 A1, and copending, commonly assigned U.S. patent application Ser. No. 10/745,352 filed Dec. 12, 2003, entitled Gels from Controlled Distribution Block Copolymers, now published as US2004/0138371 A1, which is a continuation-in-part of U.S. patent application Ser. No. 10/359,462, and copending, commonly assigned U.S. patent application Ser. No. 10/681,608 filed Oct. 8, 2003 entitled Photopolymerizable Compositions and Flexographic Printing Plates Prepared from Controlled Distribution Block Copolymers, now published as US2004/0072951, all of which claim the benefit of U.S. Provisional Patent Application Ser. No. 60/355,210 filed Feb. 7, 2002.

SUMM This invention relates to gels prepared from novel anionic block copolymers of mono alkenyl arenes and conjugated dienes.

SUMM The preparation of block copolymers of mono alkenyl arenes and conjugated dienes is well known. One of the first patents on linear ABA block copolymers made with styrene and butadiene is U.S. Pat. No. 3,149,182. These polymers in turn could be hydrogenated to form more stable block copolymers, such as those described in U.S. Pat. No. 3,595,942 and U.S. Pat. No. Re. 27,145. Such polymers are broadly termed Styrenic Block Copolymers or SBC's.

Now a novel anionic block copolymer based on mono alkenyl arene end blocks and controlled distribution mid blocks of mono alkenyl arenes and conjugated dienes has been discovered and is described in copending, commonly assigned U.S. patent application Ser. No. 60/355,210, entitled "NOVEL BLOCK COPOLYMERS AND METHOD FOR MAKING SAME". Methods for making such polymers are described in detail in the above-mentioned patent application. Patentees have found that these new polymers will allow the preparation of improved oil gels. In particular, this invention comprises a new class of SBC's in which the polymer manufacturer can vary the compatibility characteristics of the rubber segment, resulting in improved oil gels.

SUMM In one aspect of the present invention we have discovered a novel oil gel composition comprising 100 parts by weight of at least one hydrogenated block copolymer having a controlled distribution block of a mono alkenyl arene and conjugated diene and 350 to 2000 parts by weight of an extender oil. The hydrogenated block copolymer has at least one polymer block A and at least one polymer block B wherein (a.) prior to hydrogenation each A block is a mono alkenyl arene homopolymer block and each B block is a controlled distribution copolymer block of at least one conjugated diene and at least one mono alkenyl arene; (b.) subsequent to hydrogenation about 0-10% of the arene double bonds have been reduced, and at least about 90% of the conjugated diene double bonds have been reduced; (c.) each A block having a number average molecular weight between about 3,000 and about 60,000 and each B block having a number average molecular weight between about 30,000 and about 300,000; (d.) each B block comprises terminal regions adjacent to the A blocks that are rich in conjugated diene units and one or more regions not adjacent to the A blocks that are rich in mono alkenyl arene units; (e.) the total amount of mono alkenyl arene in the hydrogenated block copolymer is about 20 percent weight to about 80 percent weight; and (f.) the weight percent of mono alkenyl arene in each B block is between about 10 percent and about 75 percent. The general configuration of the block copolymer is A-B, A-B-A, (A-B).sub.n, (A-B).sub.n-A, (A-B-A).sub.nX, (A-B).sub.nX or a mixture thereof, where n is an integer from 2 to about 30, preferably 2to about 15, more preferably 2 to about 6, and X is coupling agent residue.

DETD The key component of the present invention is the novel block copolymer containing mono alkenyl arene end blocks and a unique mid block of a mono alkenyl arene and a conjugated diene. Surprisingly, the combination of (1) a unique control for the monomer addition and (2) the use of diethyl ether or other modifiers as a component of the solvent (which will be referred to as "distribution agents") results in a certain characteristic distribution of the two monomers (herein termed a "controlled distribution" polymerization, i.e., a polymerization resulting in a "controlled distribution" structure), and also results in the presence of certain mono alkenyl arene rich regions and certain conjugated diene rich regions in the polymer block. For purposes hereof, "controlled distribution" is defined as referring to a molecular structure having the following attributes: (1) terminal regions adjacent to the mono alkenyl arene homopolymer ("A") blocks that are rich in (i.e., having a greater than average amount of) conjugated diene units; (2) one or more regions not adjacent to the A blocks that are rich in (i.e., having a greater than average number of) mono alkenyl arene units; and (3) an overall structure having relatively low blockiness. For the purposes hereof, "rich in" is defined as greater than the average amount, preferably greater than 5% of the average amount. This relatively low blockiness can be shown by either the presence of only a single glass transition temperature (Tg) intermediate between the Tg's of either monomer alone, when analyzed using differential scanning calorimetry ("DSC") thermal methods or via mechanical methods, or as shown via proton nuclear magnetic resonance ("H-NMR") methods. The potential for blockiness can also be inferred from measurement of the UV-visible absorbance in a wavelength range suitable for the detection of polystyryllithium end groups during the polymerization of the B block. A sharp and substantial

increase in this value is indicative of a substantial increase in polystyryllithium chain ends. In this process, this will only occur if the conjugated diene concentration drops below the critical level to maintain controlled distribution polymerization. Any styrene monomer that is present at this point will add in a blocky fashion. The term "styrene blockiness", as measured by those skilled in the art using proton NMR, is defined to be the proportion of S units in the polymer having two S nearest neighbors on the polymer chain. The styrene blockiness is determined after using H-1 NMR to measure two experimental quantities as follows:

- DETD In a preferred embodiment of the present invention, the subject controlled distribution copolymer block has two distinct types of regions—conjugated diene rich regions on the ends of the block and a mono alkenyl arene rich region near the middle or center of the block. What is desired is a mono alkenyl arene/conjugated diene controlled distribution copolymer block, wherein the proportion of mono alkenyl arene units increases gradually to a maximum near the middle or center of the block and then decreases gradually until the polymer block is fully polymerized. This structure is distinct and different from the tapered and/or random structures discussed in the prior art.
- DETD It is also important to control the molecular weight of the various blocks. For an AB diblock, desired block weights are 3,000 to about 60,000 for the mono alkenyl arene A block, and 30,000 to about 300,000 for the controlled distribution conjugated diene /mono alkenyl arene B block. Preferred ranges are 5000 to 45,000 for the A block and 50,000 to about 250,000 for the B block. For the triblock, which may be a sequential ABA or coupled (AB).sub.2 X block copolymer, the A blocks should be 3,000 to about 60,000, preferably 5000 to about 45,000, while the B block for the sequential block should be about 30,000 to about 300,000, and the B blocks (two) for the coupled polymer half that amount. The total average molecular weight for the triblock copolymer should be from about 40,000 to about 400,000, and for the radial copolymer from about 60,000 to about 600,000. These molecular weights are most accurately determined by light scattering measurements, and are expressed as number average molecular weights.
- Another important aspect of the present invention is to control the microstructure or vinyl content of the conjugated diene in the controlled distribution copolymer block. The term "vinyl content" refers to a conjugated diene which is polymerized via 1,2-addition (in the case of butadiene--it would be 3,4-addition in the case of isoprene). Although a pure "vinyl" group is formed only in the case of 1,2-addition polymerization of 1,3butadiene, the effects of 3,4-addition polymerization of isoprene (and similar addition for other conjugated dienes) on the final properties of the block copolymer will be similar. The term "vinyl" refers to the presence of a pendant vinyl group on the polymer chain. When referring to the use of butadiene as the conjugated diene, it is preferred that about 20 to about 80 mol percent of the condensed butadiene units in the copolymer block have 1,2 vinyl configuration as determined by proton NMR analysis, preferably about 30 to about 70 mol percent of the condensed butadiene units should have 1,2-vinyl configuration. This is effectively controlled by varying the relative amount of the distribution agent. As will be appreciated, the distribution agent serves two purposes -- it creates the controlled distribution of the mono

alkenyl arene and conjugated diene, and also controls the microstructure of the conjugated diene. Suitable ratios of distribution agent to lithium are disclosed and taught in U.S. Pat. No. Re. 27,145, which disclosure is incorporated by reference.

The block copolymer is selectively hydrogenated. DETD Hydrogenation can be carried out via any of the several hydrogenation or selective hydrogenation processes known in the prior art. For example, such hydrogenation has been accomplished using methods such as those taught in, for example, U.S. Pat. Nos. 3,494,942; 3,634,594; 3,670,054; 3,700,633; and U.S. Pat. No. Re. 27,145. Hydrogenation can be carried out under such conditions that at least about 90 percent of the conjugated diene double bonds have been reduced, and between zero and 10 percent of the arene double bonds have been reduced. Preferred ranges are at least about 95 percent of the conjugated diene double bonds reduced, and more preferably about 98 percent of the conjugated diene double bonds are reduced. Alternatively, it is possible to hydrogenate the polymer such that aromatic unsaturation is also reduced beyond the 10 percent level mentioned above. In that case, the double bonds of both the conjugated diene and arene may be reduced by 90 percent or more.

DETD In an alternative, the block copolymer of the present invention may be functionalized in a number of ways. One way is by treatment with an unsaturated monomer having one or more functional groups or their derivatives, such as carboxylic acid groups and their salts, anhydrides, esters, imide groups, amide groups, and acid chlorides. The preferred monomers to be grafted onto the block copolymers are maleic anhydride, maleic acid, fumaric acid, and their derivatives. A further description of functionalizing such block copolymers can be found in Gergen et al, U.S. Pat. Nos. 4,578,429 and in 5,506,299. In another manner the selectively hydrogenated block copolymer of the present invention may be functionalized by grafting silicon or boron containing compounds to the polymer as taught in U.S. Pat. No. 4,882,384. In still another manner, the block copolymer of the present invention may be contacted with an alkoxy-silane compound to form silane-modified block copolymer. In yet another manner, the block copolymer of the present invention may be functionalized by reacting at least one ethylene oxide molecule to the polymer as taught in U.S. Pat. No. 4,898,914, or by reacting the polymer with carbon dioxide as taught in U.S. Pat. No. 4,970,265. Still further, the block copolymers of the present invention may be metallated as taught in U.S. Pat. Nos. 5,206,300 and 5,276,101, wherein the polymer is contacted with an alkali metal alkyl, such as a lithium alkyl. And still further, the block copolymers of the present invention may be functionalized by grafting sulfonic groups to the polymer as taught in U.S. Pat. No. 5,516,831.

DETD Controlled distribution block copolymers of the present invention were prepared according to the process disclosed in copending patent application Ser. No. 60/355,210 referenced above, including it's continuing application filed concurrently. The polymers were selectively hydrogenated ABA block copolymers where the A blocks were polystyrene blocks and the B block prior to hydrogenation was a styrene butadiene controlled distribution block having terminal regions that are rich in butadiene units and a center region that was rich in styrene units. The polymers are shown in Table 1 below. Step I MW is the molecular weight of the first A block, Step II MW is the molecular

weight of the AB blocks and Step III MW is the molecular weight of the ABA blocks. The polymers were hydrogenated such that greater than about 95% of the diene double bonds have been reduced. What is claimed is:

CLM

1. An oil gel composition comprising 100 parts by weight of at least one hydrogenated block copolymer and from about 400 to about 2000 parts by weight of an extending oil, wherein said hydrogenated block copolymer has at least one polymer block A and at least one polymer block B, and wherein: a. prior to hydrogenation each A block is a mono alkenyl arene homopolymer block and each B block is a controlled distribution copolymer block of at least one conjugated diene and at least one mono alkenyl arene; b. subsequent to hydrogenation about 0-10% of the arene double bonds have been reduced, and at least about 90% of the conjugated diene double bonds have been reduced; c. each A block having a number average molecular weight between about 3,000 and about 60,000 and each B block having a number average molecular weight between about 20,000 and about 300,000; d. each B block comprises terminal regions adjacent to the A blocks that are rich in conjugated diene units and one or more regions not adjacent to the A blocks that are rich in mono alkenyl arene units; e. the total amount of mono alkenyl arene in the hydrogenated block copolymer is about 20 percent weight to about 80 percent weight; and f. the weight percent of mono alkenyl arene in each B block is between about 10 percent and about 75 percent.

CLMWhat is claimed is:

5. The oil gel composition according to claim 4 wherein the polymer is an ABA polymer and each block B has a center region with a minimum ratio of butadiene units to styrene units.

CLM What is claimed is:

8. The oil gel composition according to claim 7 wherein said hydrogenated block copolymer is a linear hydrogenated ABA styrene/butadiene block copolymer having a total number average molecular weight of about 80,000 to about 140,000.

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ANSWER 5 OF 9 USPAT2 on STN

2005:275365 USPAT2 ACCESSION NUMBER:

TITLE: Photocurable compositions and flexographic printing

plates comprising the same

INVENTOR(S): St. Clair, David J., Houston, TX, UNITED STATES

Hansen, David R., Houston, TX, UNITED STATES Dubois, Donn A., Houston, TX, UNITED STATES
Kraton Polymers U.S. LLC, Houston, TX, UNITED STATES

PATENT ASSIGNEE(S):

(U.S. corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 7241540	В2	20070710	
APPLICATION INFO.:	US 2004-832733		20040427	(10)
DOCUMENT TYPE:	Utility			
FILE SEGMENT:	GRANTED			
PRIMARY EXAMINER:	Hamilton, Cynthia			

LEGAL REPRESENTATIVE: Masse, Michael A.

NUMBER OF CLAIMS: 13

EXEMPLARY CLAIM: 1,8,9,10,11

LINE COUNT: 561

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

The present invention relates to photocurable compositions for use in flexographic printing plates comprising selectively hydrogenated block copolymers of conjugated dienes and monoalkenyl arenes and flexographic printing plates made from the same. The block copolymers, either linear or radial, have terminal blocks of unsaturated conjugated diene. The block copolymer is further comprised of monoalkenyl arene blocks and hydrogenated conjugated diene blocks. The compositions exhibit exceptional improvement in degree of cure over comparative selectively hydrogenated block copolymers.

SUMM Unhydrogenated styrene diene block copolymers, both the SIS and SBS types, can be used to make UV cured, flexographic printing plates as taught in U.S. Pat. No. 4,427,759. Although they are widely used and give excellent performance, one limitation is that the plates made with the unsaturated polymers have limited resistance to degradation by ozone. This is becoming more of a problem as UV cured inks become more widely used since ozone is generated from oxygen during the UV irradiation used to cure the ink.

Now an improved photocurable composition based on selectively hydrogenated block copolymers having both hydrogenated conjugated diene blocks and unsaturated conjugated diene blocks has been found. This improved composition leads to high gel contents, or degree of cure, after photocure. The higher gel content is expected to result in improved resolution and dimensional stability of the flexographic printing plate. Furthermore, the selectively hydrogenated character of the block copolymer comprising the photocurable composition is expected to be resistant to ozone generated during photocure of the flexographic plate itself and of UV curable inks.

SUMM In one aspect the invention is a photocurable composition comprising: a) from 80 to 90% by weight of a selectively hydrogenated block copolymer having at least one hydrogenated polybutadiene block (EB), at least two polymeric monovinyl aromatic hydrocarbon blocks (S), and at least one polymeric conjugated diene block (I) wherein the I block is a terminal block and is attached to an S block; from 5 to 15% by weight of an acrylic crosslinker; from 0 to 10% by weight of a softening oil; and from 0.5 to 4% by weight of a photoinitiator.

DETD The present invention comprises a block copolymer as component (a). As used herein the block copolymer is defined as having at least two blocks of a mono alkenyl arene (S), such as styrene, and at least one block of a substantially hydrogenated conjugated diene (EB) and at least one block of a substantially unsaturated conjugated diene (I).

DETD The block copolymers are prepared using living anionic polymerization techniques commonly known. These techniques generally employ alkali metal initiations such as organo-lithium compounds. The monomers composing the conjugated diene and monoalkenyl arene blocks can be selected from the general class of anionically polymerizable monomers. In particular, the conjugated diene monomers for use herein are 1

,3-butadiene, commonly referred to as butadiene, and substituted butadiene such as isoprene, piperylene, 2,3-dimethyl-1,3-butadiene, and 1-phenyl-1,3-butadiene, or mixtures thereof. Most preferred in the present invention are butadiene and isoprene. The monovinyl arene monomers for use herein are styrene, alpha-methyl styrene, para-methyl styrene, vinyl toluene, vinylnaphthalene and para-butyl styrene. In the present invention the most preferred monovinyl arene monomer is styrene
The embodiments of the present invention comprise a block

- DETD The embodiments of the present invention comprise a block copolymer composition which is a linear tetrablock, a linear pentablock, a linear multiblock, a symmetrical radial, an asymmetrical radial block copolymer, or mixtures thereof. In all cases there is at least one terminal substantially unsaturated conjugated diene block (I). The I block is attached at only one of its ends and it is attached to an S block. Furthermore, the S blocks are separated by an EB block.
- DETD It will be understood that during coupling, the coupling site is at the termini of the EB segments. The coupling process produces the final EB block by joining two or more living arms, each having EB segments. As such, the EB molecular weights herein specified refer to the hydrogenated conjugated diene molecular weight between two monoalkenyl arene S blocks. Regardless of whether the coupled polymer results from the coupling of two living arms (linear block copolymer) or more living arms, the molecular weight of the conjugated diene segments in the living arms before coupling will be half the EB molecular weight herein specified.
- DETD Another important aspect of the present invention is to control the microstructure or vinyl content of the substantially hydrogenated conjugated diene block. The term "vinyl content" refers to a conjugated diene, which is polymerized via 1,2-addition (in the case of butadiene--it would be 3,4-addition in the case of isoprene). Although a pure "vinyl" group is formed only in the case of 1,2-addition polymerization of 1,3-butadiene, the effects of 3,4-addition polymerization of isoprene (and similar addition for other conjugated dienes) on the final properties of the block copolymer will be similar. The term "vinyl" refers to the presence of a pendant vinyl group on the polymer chain. When referring to the use of butadiene as the conjugated diene, it is preferred that about 20 to about 90 mol percent of the condensed butadiene units in the copolymer block have 1,2 vinyl configuration as determined by H-1 NMR analysis, preferably about 35 to 80 mol percent of the condensed butadiene units should have 1,2-vinyl configuration. This is effectively controlled by varying the relative amount and/or type of the distribution agent. Suitable types and ratios of distribution agent to lithium polymerization initiator are disclosed and taught in U.S. Pat. No. Re. 27,145 and 5,795,944, which disclosures are incorporated by reference.
- DETD The block copolymer is selectively hydrogenated. Hydrogenation can be carried out via any of the several hydrogenation or selective hydrogenation processes known in the prior art. For example, such hydrogenation has been accomplished using methods such as those taught in, for example, U.S. Pat. Nos. 3,494,942; 3,634,549; 3,670,054; 3,700,633; and U.S. Pat. No. Re. 27,145. Hydrogenation can be carried out under such conditions that at least about 90 percent of the conjugated diene double bonds in the EB block have

been reduced, and between zero and 10 percent of the arene double bonds have been reduced. Preferred ranges are at least about 95 percent of the EB block double bonds reduced, and more preferably about 98 percent of the conjugated diene double bonds are reduced. Importantly, the hydrogenation is conducted in such a fashion to substantially hydrogenate the EB block while leaving the I block substantially unhydrogenated. Substantially hydrogenated means less than 10 mol % of the double bonds remain unsaturated. Substantially

unhydrogenated means at least 50 mol % and most preferably 50 to 90 mol

% of the original double bonds remain unsaturated.

CLM What is claimed is:

1. A photocurable composition comprising: a. from 80 to 90% by weight of a selectively hydrogenated block copolymer having at least one hydrogenated poly(conjugated diene) block (EB), at least two polymeric monoalkenyl arene blocks (S), and at least one polymeric conjugated diene block (I) wherein the I block is a terminal block and is attached to an S block; and, b. from 5 to 15% by weight of an acrylic crosslinker; and c. from 0 to 10% by weight of a softening oil; and d. from 0.5 to 4% by weight of a photoinitiator wherein the block copolymer is a symmetric linear or radial polymer having the structure (I--S-EB).sub.pY and Y is the residue of a coupling agent, and p is 2 to 4.

CLM What is claimed is:

11. A photocurable composition comprising: a. from 80 to 90% by weight of a selectively hydrogenated block copolymer having at least one hydrogenated poly(conjugated diene) block (EB), at least two polymeric monoalkenyl arene blocks (S), and at least one polymeric conjugated diene block (I) wherein the I block is a terminal block and is attached to an S block; and, b. from 5 to 15% by weight of an acrylic crosslinker; and c. from 0 to 10% by weight of a softening oil; and d. from 0.5 to 4% by weight of a photoinitiator wherein the block copolymer is a linear tetrablock having the structure I-S-EB-S.

CLM What is claimed is:

13. A photocurable composition comprising: a. from 80 to 90% by weight of a selectively hydrogenated block copolymer having at least one hydrogenated poly(conjugated diene) block (EB), at least two polymeric monoalkenyl arene blocks (S), and at least one polymeric conjugated diene block (I) wherein the I block is a terminal block and is attached to an S block; and, b. from 5 to 15% by weight of an acrylic crosslinker; and c. from 0 to 10% by weight of a softening oil; and d. from 0.5 to 4% by weight of a photoinitiator wherein the block copolymer is an asymmetric radial block copolymer having a structure (I--S-EB).sub.qY(EB-S).sub.r wherein, on average, q is at least 1 and (q+r) is 2 to 4.

=> d 15 3 ibib hit

L5 ANSWER 3 OF 9 USPATFULL on STN

ACCESSION NUMBER: 93:91503 USPATFULL

TITLE: Electrophotographic lithographic printing plate

precursor

INVENTOR(S): Kato, Eiichi, Shizuoka, Japan

PATENT ASSIGNEE(S): Fuji Photo Film Co., Ltd., Kanagawa, Japan (non-U.S.

corporation)

NUMBER KIND DATE ______

PATENT INFORMATION: US 5258249 19931102 APPLICATION INFO.: US 1991-779915 19911021 19911021 (7)

DISCLAIMER DATE: 20101019

> NUMBER DATE _____

PRIORITY INFORMATION: JP 1990-302480 19901109

DOCUMENT TYPE: Utility

FILE SEGMENT: Granted
PRIMARY EXAMINER: McCamish, Marion E.
ASSISTANT EXAMINER: Crossan, Stephen C.

LEGAL REPRESENTATIVE: Sughrue, Mion, Zinn, Macpeak & Seas

NUMBER OF CLAIMS: 11 NUMBER OF CLAIM: 1
EXEMPLARY CLAIM: 1
1554

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

The AB block copolymer used in the present invention can be produced by a conventionally known synthesis method. More specifically, it can be produced by a known polymerization reaction, for example, an ion polymerization reaction with an organic metal compound (e.g., alkyl lithiums, lithium diisopropylamide, and alkylmagnesium halides) or a hydrogen iodide/iodine system, a photopolymerization reaction using a porphyrin metal complex as a catalyst, or a group transfer polymerization reaction.

SUMM Resins used together with the AB block copolymer according to the present invention include alkyd resins, vinyl acetate resins, polyester resins, styrene-butadiene resins, and acryl resins, and more specifically, those described, for example, in Ryuji Kurita & Jiro Ishiwatari, Kobunshi, 17, 278 (1968), Harumi Miyamoto & Hidehiko Takei, Imaging, No. 8, 9 (1973).

A mixed solution of 30 g of the above described polymer, 20 g of DETD tri(isopropyl)silyl methacrylate and 33.3 g of tetrahydrofuran was heated to 50° C. under nitrogen gas stream and irradiated under the same condition as above for 16 hours to conduct polymerization. To the reaction mixture was added 80 g of tetrahydrofuran to dissolve, the resulting solution was reprecipitated from 1.0 liter of methanol, and the precipitates were collected and dried. A weight average molecular weight of the block copolymer thus obtained was 4.5+10.sup.4.

=> FIL STNGUIDE SINCE FILE TOTAL ENTRY SESSION 115.01 115.22 COST IN U.S. DOLLARS FULL ESTIMATED COST SINCE FILE TOTAL SESSION -0.80 -0.80 DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS) CA SUBSCRIBER PRICE

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L2

T.3

T.4

L5

(FILE 'HOME' ENTERED AT 18:27:29 ON 01 JUN 2008)
SET ABBR ON PERM
SET PLURALS ON PERM

FILE 'USPATFULL, USPATOLD, USPAT2, CAPLUS, JAPIO' ENTERED AT 18:28:00 ON 01 JUN 2008

L1 2004 SEA ABB=ON PLU=ON (IRRADIAT? OR PHOTOPOLYMERI?)(S)(BLOCK(3A) COPOLYMER?)

2383 SEA ABB=ON PLU=ON ((POLYMER# OR COPOLYMER#)(4A)(BLOCK# OR SEGMENT#))(S)((ORTHO? OR META? OR PARA?)(3A)(ALKYL? OR METHYL? OR ETHYL?))

45 SEA ABB=ON PLU=ON L1 AND L2

47954 SEA ABB=ON PLU=ON ((POLYMER# OR COPOLYMER#)(4A)(BLOCK# OR SEGMENT#))(S)(CONJUGATED DIEN? OR BUTADIENE OR 1,3-BUTADIENE OR ISOPRENE)

9 SEA ABB=ON PLU=ON L3 AND L4

D L5 1-9 IBIB ABS

D L5 8 IBIB HIT

D L5 7 IBIB HIT

D L5 8 IBIB HIT

D L5 5 IBIB HIT

D L5 3 IBIB HIT

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FILE USPATFULL

FILE COVERS 1971 TO PATENT PUBLICATION DATE: 29 May 2008 (20080529/PD)

FILE LAST UPDATED: 29 May 2008 (20080529/ED)

HIGHEST GRANTED PATENT NUMBER: US7380282

HIGHEST APPLICATION PUBLICATION NUMBER: US2008127393

CA INDEXING IS CURRENT THROUGH 29 May 2008 (20080529/UPCA)

ISSUE CLASS FIELDS (/INCL) CURRENT THROUGH: 29 May 2008 (20080529/PD)

REVISED CLASS FIELDS (/NCL) LAST RELOADED: Apr 2008

USPTO MANUAL OF CLASSIFICATIONS THESAURUS ISSUE DATE: Apr 2008

FILE USPATOLD

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FILE USPAT2

FILE COVERS 2001 TO PUBLICATION DATE: 29 May 2008 (20080529/PD) FILE LAST UPDATED: 29 May 2008 (20080529/ED) HIGHEST GRANTED PATENT NUMBER: US2008007718 HIGHEST APPLICATION PUBLICATION NUMBER: US2008126760

CA INDEXING IS CURRENT THROUGH 29 May 2008 (20080529/UPCA) ISSUE CLASS FIELDS (/INCL) CURRENT THROUGH: 29 May 2008 (20080529/PD) REVISED CLASS FIELDS (/NCL) LAST RELOADED: Apr 2008 USPTO MANUAL OF CLASSIFICATIONS THESAURUS ISSUE DATE: Apr 2008

FILE CAPLUS

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FILE COVERS 1907 - 1 Jun 2008 VOL 148 ISS 23 FILE LAST UPDATED: 30 May 2008 (20080530/ED)

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FILE JAPIO

<20080507/UP> FILE LAST UPDATED: 07 MAY 2008 MOST RECENT PUBLICATION DATE: 31 JAN 2008

>>> GRAPHIC IMAGES AVAILABLE <<<

FILE STNGUIDE

FILE CONTAINS CURRENT INFORMATION.

LAST RELOADED: May 30, 2008 (20080530/UP).

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